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Laughner

[11] **Patent Number:** **5,461,092**[45] **Date of Patent:** **Oct. 24, 1995**[54] **POLYCARBONATE/AROMATIC POLYESTER
BLENDS MODIFIED WITH AN
EPOXIDE-CONTAINING COPOLYMER**

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[75] **Inventor:** **Michael K. Laughner**, Lake Jackson, Tex.**FOREIGN PATENT DOCUMENTS**[73] **Assignee:** **The Dow Chemical Company**, Midland, Mich.

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[21] **Appl. No.:** **345,885**[22] **Filed:** **Nov. 28, 1994****Related U.S. Application Data****OTHER PUBLICATIONS**

[63] Continuation of Ser. No. 960,482, Oct. 9, 1992, Pat. No. 5,369,154, which is a continuation-in-part of Ser. No. 703,934, May 22, 1991, abandoned, which is a continuation-in-part of Ser. No. 508,997, Apr. 12, 1990, abandoned.

Abstract of "The Mechanical Properties of Elastomer Modified Polycarbonate/Poly(ethylene terephthalate) Blend" by Liao, Guo and Chang, p. 791, Proceedings of the 13th R.O.C. Polymer Symposium, 1990.

[51] **Int. Cl.⁶** **C08L 69/00; C08L 67/02**
[52] **U.S. Cl.** **523/436; 524/445; 524/449; 524/451; 524/504; 524/508; 525/67; 525/133; 525/148**

Abstract of "The Mechanical Properties of Elastomer Modified Polycarbonate/Poly(ethylene terephthalate) Blend" by Liao, Guo and Chang, p. 1009, Proceedings of the 1990 Annual Conference of the Chinese Society of Material Science, 1990.

[58] **Field of Search** **525/67, 133, 148; 524/445, 449, 451, 504, 508; 523/436**Derwent Abstract No. 87-207,007.
Derwent Abstract No. 87-266,737.
Derwent Abstract No. 89-107,951.
Derwent Abstract No. 90-140,501.[56] **References Cited****U.S. PATENT DOCUMENTS***Primary Examiner*—David Buttner

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[57] **ABSTRACT**

A polycarbonate blend of good impact and flexural strength, good heat distortion and weldline properties, and good solvent resistance prepared by admixing with polycarbonate an aromatic polyester, an olefinic epoxide-containing modifier, and a rubber-modified styrene/acrylonitrile copolymer.

20 Claims, No Drawings

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**POLYCARBONATE/AROMATIC POLYESTER
BLENDS MODIFIED WITH AN
EPOXIDE-CONTAINING COPOLYMER**

This application is a continuation of Ser. No. 07/960,482, filed Oct. 9, 1992 now U.S. Pat. NO. 5,369,154, which is a continuation-in-part of Ser. No. 07/703,934, filed May 22, 1991, now abandoned, which is a continuation-in-part of Ser. No. 07/508,997, filed Apr. 12, 1990 now abandoned.

FIELD OF THE INVENTION

This invention relates to blends of polycarbonate and polyester, and relates particularly to polycarbonate/polyester blends which, when molded, display a desirably high level solvent resistance and impact and flexural strength.

BACKGROUND OF THE INVENTION

Polycarbonate has found many uses because, in general, it combines a high level of heat resistance and dimensional stability with good insulating and non-corrosive properties, and it is easily molded. However, its ductility is often reduced by contact with organic solvents such as gasoline. In blends of polycarbonate with other polymers such as polyester, especially in those blends also modified with an epoxide-containing copolymer, a balance of properties is consequently sought for the purpose of arriving at a useful level of both impact and solvent resistance.

References are known which disclose compositions of polycarbonate, polyester, an epoxide-containing copolymer modifier and a rubber-modified styrene/acrylonitrile copolymer. Among these are Akagi, JP 62-184,051, which discloses a 5-component system such as compositions containing polyester, polycarbonate, butadiene-based graft copolymer, ethylenic copolymer, and glycidyl ester copolymers. Other references such as Taubitz, U.S. Pat. No. 4,774,286; Lausberg, U.S. Pat. No. 4,912,163; and Chung U.S. Pat. No. 4,554,315 disclose a 4-component system of polyester, polycarbonate, butadiene-based graft copolymer, and glycidyl ester copolymers, but describe a butadiene-based graft copolymer, as a component therein, as having greater than 25 percent rubber by weight.

It has been found, however, that the use a rubber-modified styrene/acrylonitrile copolymer which contains 1-25 percent rubber by weight in a blend of polycarbonate, polyester and an epoxide-containing modifier results in a composition which, when molded, possesses a good balance of processing and physical properties, for example a desirably high level of solvent and impact resistance. This is surprisingly accomplished at a relatively low rubber content and without the use of impact modifiers other than the rubber-modified styrene/acrylonitrile copolymer.

SUMMARY OF THE INVENTION

In one aspect, this invention involves a composition of matter which contains

- (a) an aromatic polycarbonate,
- (b) a crystalline aromatic polyester,
- (c) a thermoplastic epoxide-containing copolymer, having a glass transition temperature of less than 0° C. prepared from (i) one or more olefin monomers, and (ii) at least one vinyl monomer carrying at least one epoxide group, and
- (d) a rubber-modified styrene/acrylonitrile copolymer containing 1-25 percent rubber by weight.

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The compositions of this invention are useful, for example, in the production of films, fibers, extruded sheets, multi-layer laminates and molded or shaped articles of virtually all varieties, especially appliance and instrument housings, automobile body panels and other components for use in the automotive and electronics industries. The methods of this invention are useful for preparing compositions and molded articles having applications which are the same as or similar to the foregoing.

**DETAILED DESCRIPTION OF THE
INVENTION**

The compositions of this invention are those in which (a) polycarbonate has been admixed in a blended composition with (b) a crystalline aromatic polyester, (c) an olefinic epoxide-containing modifier having a Tg less than 0° C., and (d) a rubber-modified styrene/acrylonitrile copolymer containing 1-25 weight-percent rubber. Suitable ranges of content for components (a), (b), (c), and (d) in the compositions of this invention, expressed in percent of the total weight of all components present in the composition, are as follows:

- (a) polycarbonate from about 5 percent to about 95 percent, and preferably from about 10 percent to about 85 percent;
- (b) crystalline aromatic polyester from about 5 percent to about 95 percent, and preferably from about 10 percent to about 70 percent;
- (c) epoxide-containing modifier from about 0.1 percent to about 20 percent, and preferably from about 1 percent to about 15 percent; and
- (d) rubber-modified styrene/acrylonitrile copolymer from about 1 percent to about 50 percent, and preferably from about 1 percent to about 25 percent.

Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically the substances to be admixed with polycarbonate are dry blended in particulate form with sufficient agitation to obtain thorough distribution thereof within the polycarbonate. If desired, the dry-blended formulation can further, but need not, be melt mixed in an extruder. Mixing rolls, a dough-mixer or a Banbury mixer can also be used in the blending. Alternatively, a master batch formulation can be prepared containing polycarbonate or polyester and the substances to be admixed or blended with it wherein polycarbonate or polyester is present in only a minor proportion, for example 20 percent. The master batch is then available for storage or shipment in commerce, and can be diluted with additional polycarbonate or polyester at the time of use. The compositions of this invention can be formed or molded using conventional techniques such as compression, injection, calendaring, vacuum forming, extrusion and/or blow molding techniques, alone or in combination. The compositions can also be formed into films, fibers, multi-layer laminates or extruded sheets on any machine suitable for such purpose.

Component (a), the polycarbonates suitable for use in the present invention are those which have a glass transition temperature exceeding 135° C., and they may be produced by any of the conventional processes known in the art for the manufacture of polycarbonates. Generally, aromatic polycarbonates are prepared by reacting an aromatic dihydric phenol with a carbonate precursor, such as phosgene, a haloformate or a carbonate ester.

A preferred method for preparing suitable polycarbonates involves the use of a carbonyl halide, such as phosgene, as

the carbonate precursor. This method involves passing phosgene gas into a reaction mixture containing an activated dihydric phenol, or a nonactivated dihydric phenol and an acid acceptor, such as pyridine, dimethyl aniline, quinoline and the like. The acid acceptor may be used undiluted or diluted with inert organic solvents, such as methylene chloride, chlorobenzene or 1,2-dichloroethane. Tertiary amines are advantageous since they are good solvents as well as acid acceptors during the reaction.

Yet another method for preparing such aromatic polycarbonates involves the phosgenation of an agitated suspension of an anhydrous alkali salt of an aryl diol in a nonaqueous medium such as benzene, chlorobenzene or toluene. The reaction is illustrated by the addition of phosgene to a slurry of the sodium salt of, for example, Bisphenol A in an inert polymer solvent such as chlorobenzene.

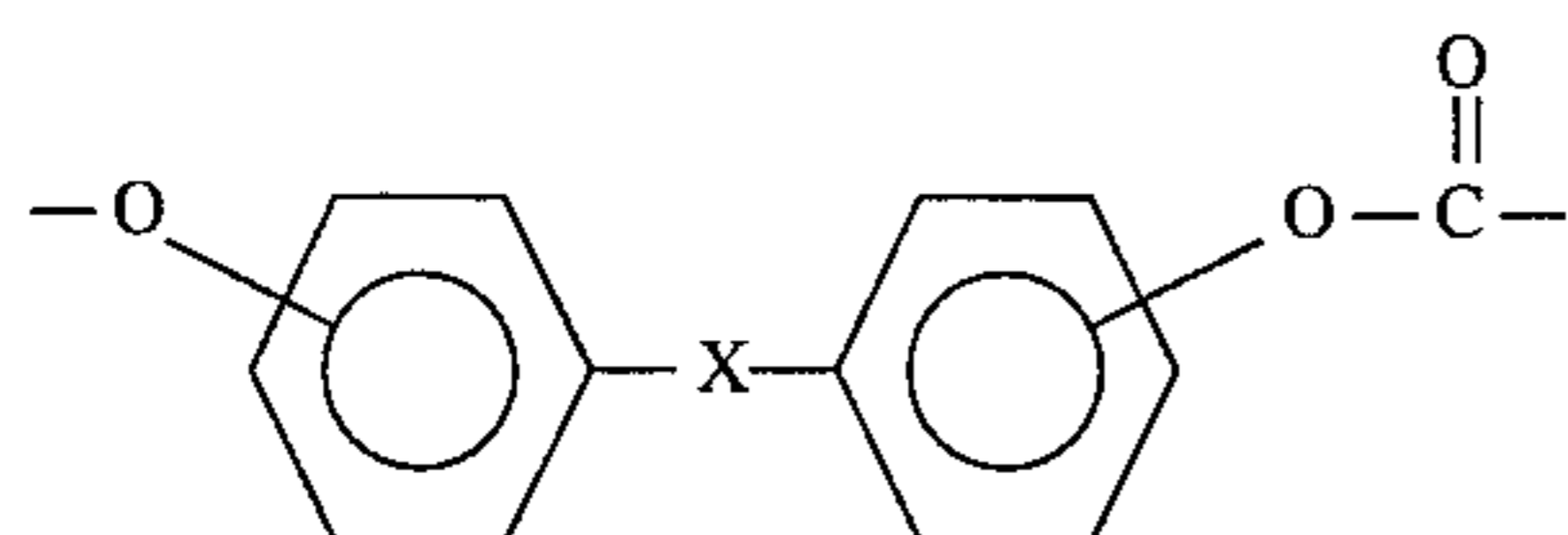
Generally speaking, a haloformate such as the bis-haloformate of Bisphenol A may be used in place of phosgene as the carbonate precursor in any of the methods described above.

When a carbonate ester is used as the carbonate precursor in the polycarbonate-forming reaction, the materials are reacted at temperatures in excess of 100° C. for times varying from 1 to 15 hours. Under such conditions, ester interchange occurs between the carbonate ester and the dihydric phenol used. The ester interchange is advantageously consummated at reduced pressures on the order of from about 10 to about 100 millimeters of mercury, preferably in an inert atmosphere such as nitrogen or argon. Although the polymer-forming reaction may be conducted in the absence of a catalyst, one may, if desired, employ a typical ester exchange catalyst, such as metallic lithium, potassium, calcium or magnesium. The amount of such catalyst, if used, is usually small, ranging from about 0.001% to about 0.1%, based on the weight of the dihydric phenols employed.

In the solution methods of preparation, the aromatic polycarbonate emerges from the reaction in either a true or pseudo solution depending on whether an aqueous base or pyridine is used as an acid acceptor. The copolymer may be precipitated from the solution by adding a polymer nonsolvent, such as heptane or isopropanol. Alternatively, the polymer solution may be heated, typically under reduced pressure, to evaporate the solvent.

The methods and reactants described above for preparing carbonate polymers suitable for use in the practice of this invention are discussed in greater detail in Schnell, U.S. Pat. No. 3,028,365; Campbell, U.S. Pat. No. 4,384,108; Glass, U.S. Pat. No. 4,529,791; and Grigo, U.S. Pat. No. 4,677,162, each being incorporated as a part hereof.

A preferred aromatic polycarbonate is characterized by repeated units corresponding to the general formula:



wherein X is a divalent, linear or cyclic C₁-C₁₅ hydrocarbon radical, a single bond, —O—, —S—, —S₂—, —SO—, —SO₂—, or —CO—. Each aromatic ring may additionally contain, instead of hydrogen, up to four substituents such as C₁-C₄ alkyl hydrocarbon or alkoxy radicals, aryl or aryloxy radicals, or halo radicals.

Although the polycarbonates mentioned above, such as those derived from 2,2-bis(4-hydroxyphenyl)propane

("Bisphenol-A" or "Bis-A"), 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-A-P" or "Bis-A-P") or Bis(hydroxyphenyl) fluorene, can each be employed in this invention as a homopolymer, the carbonate polymers used herein can also be derived from two or more bisphenols, or two or more acid- or hydroxy-terminated reactants such as dicarboxylic acids or alkylene glycols, or from two or more different dihydroxy compounds, or mixtures of any of the foregoing, in the event a carbonate copolymer or in polymer, such as a copolyester/carbonate is desired, rather than a homopolymer.

Copolymers can be formed, for example, when a bisphenol is reacted with a carbonic acid derivative and a polydiorganosiloxane containing α , ω -bishydroxyaryloxy terminal groups to yield a siloxane/carbonate block copolymer [as are discussed in greater detail in Paul, U.S. Pat. No. 4,569,970, incorporated as a part hereof], or when a bisphenol is reacted with a bis(ar-haloformylaryl) carbonate to yield an alternating copolyestercarbonate. The bis(ar-haloformylaryl) carbonate is formed by reacting a hydroxycarboxylic acid with a carbonic acid derivative under carbonate forming conditions, and the copolyestercarbonates are discussed in greater detail in Swart, U.S. Pat. No. 4,105,533, incorporated as a part hereof. Branched polycarbonate, which may also be useful herein, may be obtained by adding to the reaction mixture a tri- or polyfunctional monomer such as a tri- or tetrafunctional phenol or carboxylic acid (or a derivative such as an acyl halide or anhydride), a bisphenol containing carboxylic acid side groups, or a nitrogen-containing compound such as cyanuric chloride, or compounds containing a mixture of such groups. Preferred branching agents are trimellitic acid or pyromellitic dianhydride.

The term "polycarbonate" as used herein, and in the claims appended hereto, should therefore be understood to include carbonate homopolymers, carbonate copolymers (as described above), and/or blends of carbonate homopolymers and/or carbonate copolymers.

Component (b), the crystalline aromatic polyester used in this invention, may be made by a variety of methods. Although the self-esterification of hydroxycarboxylic acids is known, direct esterification, which involves the reaction of a diol with a dicarboxylic acid with the resulting elimination of water, is a more frequently used method for commercial production, giving an [-AABB-] polyester. Although the presence of a catalyst such as p-toluene sulfonic acid, a titanium alkoxide or a dialkyltin oxide is helpful, the primary driving force behind the direct esterification reaction is heat. Temperatures applied exceed the melting points of the reactants and typically approach the boiling point of the diol being used, and usually range from about 150° C. to about 280° C.

Alternatively, but in like manner, ester-forming derivatives of a dicarboxylic acid can be heated with a diol to obtain polyesters in an ester interchange reaction. Suitable acid derivatives for such purpose are esters, halides, salts or anhydrides of the acid. Diol derivatives such as an acetate can be used effectively when it is desired to conduct acidolysis.

Polyesters can also be produced by a ring-opening reaction of cyclic esters or lactones, for which organic tertiary bases and alkali and alkaline earth metals, hydrides and alkoxides can be used as initiators. Advantages offered by this type of reaction are that it can be run at lower temperatures, frequently under 100° C., and there is no need to remove a condensation product from the reaction.

Whether a polyester is crystalline or amorphous is typically a function of the symmetry of the starting materials

from which it is made. When one or more hydrogens on the diol and/or the diacid (or derivative) which are reacted to form a polyester are replaced by larger radicals such as alkyl or halogen, the intermolecular spacing of the resulting molecules may be disrupted if the presence of the substituent creates asymmetric or irregularly shaped molecules. A crystalline material may be identified by the endotherm it displays on a differential scanning calorimeter. A preferred polyester for use in this invention is a crystalline polyester having a melting point of 254°–260° C.

Suitable reactants for making the polyester used in this invention, in addition to than hydroxycarboxylic acids, are diols and dicarboxylic acids either or both of which can be aliphatic or aromatic. A polyester which is a poly(alkylene alkanedicarboxylate), a poly(alkylene phenylenedicarboxylate), a poly(phenylene alkanedicarboxylate), or a poly(phenylene phenylenedicarboxylate) is therefore appropriate for use herein. Alkyl portions of the polymer chain can be substituted with, for example, halogens, alkoxy groups or alkyl side chains and can contain divalent heteroatomic groups (such as —O—, —S— or —SO₂—) in the paraffinic segment of the chain. The chain can also contain unsaturation and non-aromatic rings. Aromatic rings can contain substituents such as halogens, alkoxy or alkyl groups, and can be joined to the polymer backbone in any ring position and directly to the alcohol or acid functionality or to intervening atoms.

Typical alkylene diols used in ester formation are the C₂–C₁₀ glycols, such as ethylene-, propylene-, and butylene glycol. Alkanedicarboxylic acids frequently used are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be, for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexane-dimethylene glycol, resorcinol, hydroquinone, 4,4'-thiodiphenol, bis-(4-hydroxyphenyl)sulfone, a dihydroxynaphthalene, a xylylene diol, or can be one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl)propane. Aromatic diacids include, for example, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid.

In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable for use in this invention, and are all included in the term "polyester". For example, use of cyclohexanedimethylol together with ethylene glycol in esterification with terephthalic acid forms a clear, amorphous copolyester ("PETG") of particular interest. Also contemplated are PCTG; liquid crystalline polyesters derived from mixtures of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and ethylene glycol; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl.

Aromatic polyesters such as the poly(alkylene phenylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention. These polyesters typically have an intrinsic viscosity between about 0.35 and about 1.2, preferably about 0.35 and 1.1, and are more easily processed than polyesters with higher intrinsic viscosities.

Methods and materials useful for the production of polyesters, as described above, are discussed in greater detail in

Whinfield, U.S. Pat. No. 2,465,319, Pengilly, U.S. Pat. No. 3,047,539 and Russell, U.S. Pat. No. 3,756,986, each of which is incorporated herein in its entirety.

Component (c), the olefinic epoxide-containing modifier used in this invention, is a polymer which has a glass transition temperature (T_g) less than 0° C. T_g is the temperature or temperature range at which a polymeric material shows an abrupt change in its physical properties, including, for example, mechanical strength. T_g can be determined by differential scanning calorimetry.

The epoxide-containing modifier of this invention is formed as a copolymer from (i) at least one olefin monomer such as ethylene, propylene, isopropylene, butylene or isobutylene, or at least one conjugated diene such as butadiene, and the like, or mixtures thereof; and (ii) at least one vinyl (i.e. olefinically unsaturated, including vinylidene) or olefin monomer carrying at least one epoxide group. Optionally, component (i) may itself be a copolymer prepared from one or more olefin monomers, such as those described above, as well as other vinyl monomer(s), but containing a sufficient amount of the olefin monomer(s) to impart a T_g of less than 0° C. to the epoxide-containing modifier. In addition to components (i) and (ii), the epoxide-containing copolymer may also be formed from a component (iii), at least one other vinyl (i.e. olefinically unsaturated, including vinylidene) monomer not carrying an epoxide group.

The epoxide-containing copolymer is a thermoplastic which is formed by polymerization through the double bond of each component (i) and each component (ii). The epoxide groups, although free to react, are not pendant as a grafted chain since components (i) and (ii) together form a generally linear polymer. Component (iii) may be copolymerized with components (i) and (ii) into the generally linear chain, or it may be grafted as a homopolymeric branch onto a generally linear chain prepared from components (i) and (ii).

Representative vinyl (i.e. olefinically unsaturated, including vinylidene) monomers useful as component (iii) in forming the polymeric epoxide-containing modifier of this invention include the following: vinyl compounds (especially when they bear a polar, electronegative group or functionality) such as vinyl toluene, alphas-methyl styrene, halogenated styrene; those containing nitrile groups such as copolymers of acrylonitrile, methacrylonitrile or alpha-halogenated acrylonitrile; a C₁–C₈ alkyl acrylate such as ethyl acrylate, butyl acrylate, hexyl acrylate or hydroxy ethyl acrylate; a C₁–C₈ alkyl methacrylate such as methyl methacrylate or hexyl methacrylate; other esters of the C₁–C₆ aliphatic or cycloaliphatic alcohols, especially the C₁–C₄ aliphatic or cycloaliphatic alcohols; an acrylic or methacrylic acid; the vinylidene monomers, especially when they bear a polar, electronegative group or functionality such as a halogen group, or an organic group having a double or triple bond such as phenyl, carboxy, cyano or the like; vinyl esters or vinyl ethers; alkenyl-aromatic compounds such as styrene and substituted derivatives thereof; maleimides; mononitriles having alpha-beta-olefinic unsaturation and lower alkyl or halogen substituents; esters of olefinically unsaturated carboxylic acids; aliphatic vinyl compounds such as vinyl chloride, vinylidene chloride, acrylic and methacrylic acid esters, amides and nitriles, vinyl acetate, vinyl propionate and vinyl benzoate; vinyl-methyl-ether, vinyl-ethyl-ether and vinyl-isobutyl-ether; and aromatic vinyl compounds such as styrene, alpha-methyl styrene, vinyl toluene, p-ethylstyrene, 2,4-dimethyl styrene, o-chlorostyrene and 2,5-dichlorostyrene; vinyl esters; vinyl ethers; alpha-olefins; vinyl toluenes; vinyl xylenes; the maleates; the fumarates; and the like; or mixtures of two or more of

any of the foregoing. In general, vinyl and vinylidene monomers from groups such as the vinyl and vinylidene-esters, -ethers, -organic acids, -aromatics, -alcohols, -anhydrides, -halides, -nitriles and -amides; or mixtures of any of the foregoing may be used. Additionally, any one or more of the foregoing monomers may be copolymerized with carbon monoxide.

Vinyl monomers such as the foregoing may also be copolymerized with the olefin/diene portion of the modifier to prepare the optional form of component (i); or, when carrying an epoxide group, may be used as component (ii).

Olefinically unsaturated monomers containing epoxide groups suitable for use as component (ii) of the polymeric modifier include, for example, glycidyl esters of unsaturated carboxylic acids (e.g. glycidyl methacrylate); glycidyl ethers of unsaturated alcohols (e.g. allyl-glycidyl-ether) and of alkenylphenols (e.g. isopropenylphenyl-glycidylether); and vinyl and allyl esters of epoxycarboxylic acids (e.g. vinyl esters of epoxidized oleic acid). In general, all compounds which contain both a polymerizable unsaturated group and reactive epoxide groups in the molecule can be used for the manufacture of the epoxide-containing modifier of the invention.

Copolymers of about 1–25% (by weight) of glycidyl methacrylate, about 40–95% of ethylene, and, optionally, up to about 40% of vinyl acetate or butyl acrylate are particularly suitable for use herein as the polymeric epoxide-containing modifier.

Copolymers containing epoxide groups may be obtained according to known processes, for example by radical polymerization in chlorobenzene at 80° C. in 50% strength solution. For instance, monomers such as those listed above are dissolved in an appropriate solvent, such as benzene, chlorobenzene or toluene, and polymerized at a temperature of about 80° C. by adding azobisisobutyronitrile, whereby oxygen is excluded. After the monomers have been reacted, the solvent used is distilled off (e.g., chlorobenzene at 100° C. and 20 torr) and the residue is dried in vacuum at 100° C. and then powdered. The epoxide-containing modifier of this invention can also be prepared in gas phase under conditions suitable for polymerizing an olefin. For example, the polymer can be made in either a tubular reactor or a stirred autoclave, where heated, pressurized feed streams of olefin or vinyl monomer gas, peroxide free-radical initiator and chain transfer agent are injected into the reaction device. The reaction of formation usually occurs at 1,500–3,000 atm (152–304 MPa) and at a temperature usually not exceeding 300° C., as known in the art.

The molecular weight of the polymeric epoxide-containing modifier is typically between about 10,000 and about 500,000, preferably between about 30,000 and about 200,000. A mixture of epoxide-containing modifiers may be used as well.

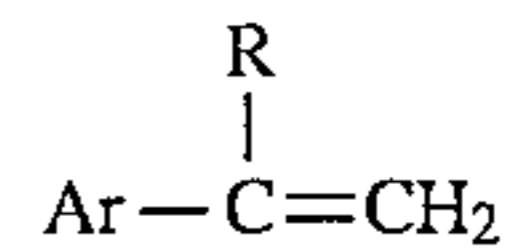
Component (d), the styrene/acrylonitrile copolymer ("SAN") suitable for use in this invention, is that which is rubber-modified. An example of a rubber-modified styrene/acrylonitrile copolymer which can be advantageously used in this invention is an elastomeric-thermoplastic composite such as an acrylonitrile-butadiene-styrene copolymer ("ABS"). The elastomeric portion of such composite is usually dispersed as discrete particles in a matrix made up of the thermoplastic portion.

ABS is typically formed by the grafting of an SAN copolymer onto a polybutadiene substrate latex. The polybutadiene forms particles of rubber—the elastomeric component—which are dispersed as a discrete phase in a thermoplastic matrix formed by the SAN. The rubber content of the

rubber-modified styrene/acrylonitrile copolymer used in this invention is 1–25% by weight, preferably 1–20% by weight, and more preferably 1–10% by weight.

This structural aspect of a rubber-modified styrene/acrylonitrile copolymer—the dispersion of rubber particles in a compatible thermoplastic phase or matrix—is more important than the precise monomer content. The composite can be manufactured from nothing other than acrylonitrile, butadiene and styrene, or other monomers can be substituted or mixed in with them. Some of the monomers which are frequently substituted for or intermixed with acrylonitrile, butadiene and styrene are mentioned below in connection with the three usual methods of manufacturing ABS. What is set forth below concerning methods of making the elastomeric/thermoplastic composite used as a rubber-modified styrene/acrylonitrile copolymer in this invention from acrylonitrile, butadiene and styrene applies equally to the other forms of said elastomeric/thermoplastic composite which result from variation in the monomer mix. The elastomeric/thermoplastic composite used as a rubber-modified styrenic thermoplastic resin in this invention can be made from any of the various monomers, and can be made by any of the various methods, which are included below in the discussion relating specifically to the manufacture of ABS.

One method for making ABS resin is emulsion polymerization wherein the first step is the production of a rubber substrate latex in an aqueous emulsion. The substrate results from polymerization, which can be initiated by organic peroxides, persulfates, iron, sugar, or peroxide redox systems, of 1,3-butadiene alone or in combination with other monomers. Butadiene can be copolymerized with either styrene or acrylonitrile to form the substrate, but numerous other comonomers yield equivalent results. In general, any mixture containing a butadiene-1,3 hydrocarbon and a copolymerizable compound containing a single olefinic double bond, in proportions such that an unsaturated elastomeric copolymer—a rubber—is formed on polymerization of the mixture in aqueous emulsion, is appropriate. For example, there may be used mixtures containing a predominant amount of butadiene-1,3, isoprene, 2,3-dimethyl butadiene-1,3 or piperylene, or a combination of two or more of these and a lesser amount of one or more of the following monomers: styrene, alpha-methyl styrene, p-methoxy styrene, p-chloro styrene, dichloro styrene, vinyl naphthalene and other alkenyl substituted aromatic compounds of the formula



wherein Ar is an aromatic radical having its connecting valence on a ring carbon atom with R being as follows: hydrogen or alkyl; acrylonitrile, methacrylonitrile, ethacrylonitrile, alphachloro acrylonitrile, methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, methyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, methyl alphachloro acrylate, methacrylamide, acrylamide, N,N-diethyl acrylamide and other nitriles, amides and alkyl esters of alpha-methylene aliphatic monocarboxylic acids; substituted aromatic maleimides such as N-phenyl maleimide; diethyl fumarate, diethylchloromaleate, vinylidene chloride, methyl vinyl ketone, methyl isopropenyl ketone, vinyl pyridines, vinyl furan, vinyl carbazole, isobutylene, ethylene, and the like. It is preferred that, in the preparation of the rubber latex, the proportion of butadiene to other monomers be in the range of about 2/1 to about 15/1.

After formation of the rubber latex substrate, the rubber latex substrate and styrene and acrylonitrile monomers are subjected to further aqueous emulsion. The concentration of styrene is usually about 1.5 to 3.5 times that of acrylonitrile. However other monomers such as methacrylonitrile, divinylbenzene, α -methyl styrene, p-methyl styrene, methyl methacrylate, N-phenyl maleimide, chlorinated and brominated styrenes, and methyl-, ethyl- or n-butylacrylate, or mixtures thereof, may also be in conjunction with styrene and acrylonitrile. Organic peroxides, azo compounds, persulfates, or redox systems are usually used to initiate polymerization. SAN is formed, some of which is grafted to the rubber latex substrate, and some of which is free. The latex containing both the grafted rubber and the free SAN is then mixed with a coagulant solution, heated and agitated to produce discrete particles of ABS resin. The slurry containing those particles is dewatered in a centrifuge, and the resin is dried. Methods for making ABS resin by emulsion polymerization, as described above, are discussed in greater detail in Childers, U.S. Pat. No. 2,820,773 and Calvert, U.S. Pat. No. 3,238,275, each being hereby incorporated as a part hereof.

When ABS is made by suspension polymerization, a pre-formed elastomeric component (i.e. a rubber), usually a polybutadiene or a butadiene/styrene copolymer, is dissolved in a mixture of styrene and acrylonitrile. The rubber component may be one of the several mentioned above with respect to emulsion polymerization of ABS, or may be polyisoprene, polycyclopentadiene, natural rubber, chlorinated rubber or copolymers of butadiene with isobutylene. However, the preferred rubber component is a linear 1,4 polybutadiene having about a 35% to 50% cis content.

The preferred ratio of styrene to acrylonitrile in the styrene-acrylonitrile solution is about 90/10 to about 60/40, and in the preferred recipe the rubber component constitutes from about 1% to less than about 40% of the product. As with the emulsion process described above, numerous substances will function in a manner equivalent to that of styrene and may be substituted therefor, to-wit: alphasubstituted styrene, or other substituted vinyl aromatics such as vinyltoluene, vinylxylene, vinyl ethyl benzene or vinylchloro benzene. Methacrylonitrile is another alkenyl cyanide monomer which will serve in the place of acrylonitrile.

The rubber component, monomers and initiator are charged to the reaction vessel and polymerization ensues until a conversion rate of about 15% to about 30% is reached, resulting in the production of a prepolymer. Phase inversion occurs, and the rubber precipitates from solution and becomes the discontinuous phase dispersed as particles ranging from 0.5 to 5 μ m in size. The prepolymer is then placed in a suspension reactor in an aqueous solution containing a suspending agent, initiator and chain transfer agent. Agitation of the solution helps complete the polymerization. The process is completed by dewatering the slurry in a centrifuge, and moisture content is further reduced by flash drying. Manufacture of ABS by the suspension process, as described above, is discussed in greater detail in Carrock, U.S. Pat. NO. 3,515,692 and Ackerman, U.S. Pat. NO. 4,151,128, each being hereby incorporated as a part hereof.

In bulk or mass polymerization, ABS is formed by dissolving an elastomeric component (i.e. a rubber) in the monomer mix, which contains styrene, acrylonitrile, an initiator and, frequently, a chain transfer agent such as a mercaptan or a terpinolene. The reaction can, however, be thermally initiated. The styrene and acrylonitrile monomers polymerize, some grafting to the rubber component, but most forming a monomer-polymer solution. As the relative

volume of the monomer-SAN polymer phase increases, discrete rubber particles become dispersed in the matrix resulting from the monomer-SAN polymer phase. The rubber particles are stabilized by being grafted to SAN polymers at the interface between the particles and the SAN polymer matrix. Additional stabilization is furnished when monomer becomes occluded, and polymerizes, within the rubber particles. Because polymerization occurs completely within a monomer/polymer medium, viscosity increases as conversion increases. To allow continued agitation of the reaction mixture despite such increasing viscosity, diluents such as methyl ethyl ketone and ethylbenzene are added to the reactor. Upon the completion of polymerization, the melt is devolatilized using equipment such as a devolatilizing extruder or a flash evaporator, and vacuum is applied to remove unreacted monomers and diluents.

As is true of ABS made by the emulsion or suspension method, numerous substances can be used in the bulk method in place of, or conjunction with, styrene, examples of such substances being as follows: alpha-alkyl monovinylidene monoaromatic compounds, e.g. alpha-methylstyrene, alpha-ethylstyrene, alpha-methylvinyltoluene; ring-substituted alkyl styrenes, e.g. vinyl toluene, o-ethylstyrene, p-ethylstyrene, 2,4-dimethylstyrene; ring-substituted halostyrenes, e.g., o-chlorostyrene, p-chlorostyrene, o-bromostyrene, 2,4-dichlorostyrene; ring-alkyl, ring-halo-substituted styrenes, e.g. 2-chloro-4-methylstyrene and 2,6-dichloro-4-methylstyrene; methacrylates such as methyl methacrylate; maleic acid and its esters and anhydrides; substituted aromatic maleimides such as N-phenyl maleimide; and mixtures of the foregoing. If so desired, mixtures of such monovinylidene aromatic monomers may be employed. Methacrylonitrile can also be used in combination with acrylonitrile. Bulk methods for the preparation of ABS, as described above, are discussed in greater detail in Kruse, U.S. Pat. No. 4,187,260, Simon, U.S. Pat. No. 4,252,911 and Weber, U.S. Pat. No. 4,526,926, each being hereby incorporated as a part hereof.

Another form which the rubber-modified styrene/acrylonitrile copolymer can take is an AES (acrylonitrile/EPDM/styrene) copolymer, which is obtained when SAN is grafted to a substrate made up of an EPDM (ethylene/propylene/non-conjugated diene) rubber. These AES copolymers are discussed in greater detail in Henton, U.S. Pat. No. 4,766,175, which is incorporated as a part hereof. SAN can also be crosslinked to an acrylate elastomer to form a rubber-modified styrene/acrylonitrile copolymer, as in the case of an ASA (acrylonitrile/styrene/ C_1 - C_8 alkyl acrylate) copolymer, which is discussed in greater detail in Yu, U.S. Pat. No. 3,944,631, being incorporated as a part hereof. Additionally, mixtures of the various copolymers described above can serve as the rubber-modified styrene/acrylonitrile copolymer of this invention.

The preferred rubber-modified styrene/acrylonitrile copolymer for use herein are ABS, AES and ASA, and the preferred ABS and AES are those which are mass produced. As the rubber particles in a mass produced rubber-modified styrene/acrylonitrile copolymer have inclusions of glassy polymer running through them, they typically have a larger volume, in relation to the amount of rubber present, than they would have in the absence of the glassy polymer inclusions. Larger particle size is advantageous when low gloss in a molded part is sought because larger particles tend to diffuse light which strikes the surface of a part rather than reflect it. A mass produced rubber-modified styrene/acrylonitrile copolymer may be distinguished from a core-shell grafted copolymeric elastomer, which is made by the emulsion process.

A variety of additives may be used in the compositions of this invention for protection against thermal, oxidative and ultra-violet degradation. Such additives may be included in the composition at any point during the processing, and the choice as to which additive is employed, if any, is not critical to this invention. Representative of the thermal and oxidative stabilizers which can advantageously be utilized are hindered phenols, hydroquinones, phosphites, including substituted members of those groups and/or mixtures of more than one thereof. A preferred phenolic antioxidant is Irganox™ 1076 anti-oxidant, available from Ciba-Geigy Corp. Ultra-violet stabilizers such as various substituted resorcinols, salicylates, benzotriazoles, benzophines, hindered amines and hindered phenols can also be usefully included in the compositions of this invention, as can be lubricants, colorants, fillers such as talc, clay or mica, pigments, ignition resistant additives and mold release agents, and reinforcement agents such as fiberglass. Additives and stabilizers such as the foregoing, and many others which have not been mentioned, are known in the art, and the decision as to which, if any, to use is not critical to this invention. However, such additives, if used, typically do not exceed 5% by weight of the total composition, except fillers or reinforcing agents, which may constitute up to 40% of the composition.

To illustrate the practice of this invention, an example of a preferred embodiment is set forth below. It is not intended, however, that this example should in any manner restrict the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of this example with those of controlled formulations (Controls A-B) which do not possess the features of, and are not therefore embodiments of, this invention.

The compositions prepared in Controls A-B and Example 1 are made by dry blending the ingredients thereof and agitating same in a paint shaker for 7 minutes. The dry blended formulations are then melt mixed in a vented 30 mm Werner-Pfleiderer co-rotating, twin screw extruder using a 270° C. set temperature and 250 rpm. Each extruded composition is passed through a water bath, chopped into granules and collected for molding. Granules are thoroughly dried in a circulated air oven at 115° C. for six hours prior to molding. All samples are prepared by injection molding on a 75 ton Arburg molding machine. Molding temperatures for the barrel and mold are set at 280° C. and 170°-190° F., respectively.

The formulations of the compositions of Controls A-B and Example 1 are shown below in Table I in parts by weight. In Table I:

“(1) PC 300-10” is Calibre® 300-10 polycarbonate resin, a 10 melt flow value polycarbonate resin having a number average molecular weight of about 9,500 and a glass transition temperature of about 148° C. available from The Dow Chemical Company;

“(2) PET 9506” is crystalline polyethylene terephthalate having 0.95 inherent viscosity (measured in accordance with ASTM Designation D 4603-86), and a melting point of 254°-260° C., available as Traytuf® polyester from Goodyear Tire and Rubber Co.;

“(3) E/VA/GMA” is a terpolymer containing ethylene, vinyl acetate and glycidyl methacrylate, available from Sumitomo Chemical America as Bondfast™ 2B copolymer, having a weight-average molecular weight of approximately 100,000;

“(4) ABS X41” is a mass produced acrylonitrile/butadiene/styrene copolymer containing approximately 20 wt% rubber, available from The Dow Chemical Company;

“(5) E/P Copolymer” is an ethylene/propylene copolymer; “(6) GRC” is a core-shell graft polymer impact modifier containing approximately 50 wt% rubber wherein styrene and acrylonitrile is grafted onto a butadiene core; and “(7) Carbon Black” is carbon black.

The results of tests performed on the compositions of Controls A-B and Example 1 are also shown below in Table I.

Impact resistance is measured by the Izod test according to ASTM Designation D 256-84 (Method A). The notch is 10 mils (0.254 mm) in radius. Weldline Izod strength is also measured according to ASTM Designation D 256-84 (Method A), but with respect to a sample which has been formed with a butt weld in a double gated mold. The sample is unnotched, and it is placed in the vise so that the weld is coincident with the top surface of the vise jaws. Izod results are reported in ft-lb/in.

The Gardner dart drop impact test is performed at 23° C. and at -30° C. by dropping a 16 pound (7.26 kg) weight which carries a ½" (12.7 mm) dart onto a circular test sample which is 2½" (63.5 mm) in diameter and ⅛" (3.175 mm) thick. The weighted dart falls freely on a slotted track and impacts the sample, which is secured in position in the path of descent on an aluminum cast base with a 0.640 inch (16.26 mm) hole to accept the dart after it impacts the sample. The instrument is a Pacific Scientific model no. IG-1120. The sample fails if it shows a crack or perforation on the side on which impact did not occur. The results are either pass (no break or perforation by the dart at the point of impact) or fail (material exhibits crack or perforation) when the dart has developed a particular amount of energy by falling from the necessary height on the track, as indicated thereon, to develop such energy. The reading recorded in Table I is the greatest amount of energy a sample could accept without failing, reported in in-lb.

Tensile properties [strength at yield (psi), strength at break (psi), percent elongation and modulus (psi×1000)] are measured in accordance with ASTM Designation D 638-84.

Flexural modulus is measured in accordance with ASTM Designation D 790-84a, and is reported in psi×1000.

Deflection temperature under load (“DTUL”) is measured in accordance with ASTM Designation D 648-82 at 264 psi, and is reported in ° C.

TABLE I

| | Example 1 | Control A | Control B |
|------------------------------|-----------|-----------|-----------|
| 1. PC 300-10 | 1300 | 1200 | 1300 |
| 2. PET 9506 | 400 | 400 | 400 |
| 3. E/VA/GMA | 100 | 100 | 100 |
| 4. ABS X41 | 200 | 200 | |
| 5. E/P Copolymer | | 100 | |
| 6. GRC | | | 200 |
| 7. Carbon Black | 0.2 | 0.2 | 0.2 |
| Weldline Izod, ft-lb/in | 5.6 | 2.4 | 29.6 |
| 23° C. Izod, ft-lb/in | 15.7 | 14.3 | 13.6 |
| 0° C. Izod, ft-lb/in | 13.6 | 7.2 | 13.1 |
| -20° C. Izod, ft-lb/in | 4.0 | 3.4 | 12.4 |
| Dart 23° C., in-lb | 389 | 318 | 319 |
| Dart -30° C., in-lb | 476 | 434 | 421 |
| <u>Tensile</u> | | | |
| Yield, psi | 7394 | 6537 | 6369 |
| Break, psi | 7567 | 6787 | 6525 |
| % Elongation | 220 | 177 | 159 |
| Modulus, psi × 1000 | 369 | 286 | 275 |
| Flexural Modulus, psi × 1000 | 325 | 290 | 265 |
| DTUL, °C. | 230 | 222 | 242 |

It can be seen from these test results that the composition of Example 1, in which the ABS copolymer contains only

about 20 wt % rubber, surprisingly achieves a desirable balance of properties compared to the control compositions despite the fact that Control A contains the additional ethylene/propylene copolymer and Control B contains an impact modifier with a much higher rubber content.

It is within the skill in the art to practice this invention in numerous modifications and variations in light of the above teachings. It is, therefore, to be understood that the various embodiments of this invention described herein may be altered without departing from the spirit and scope of this invention as defined by the appended claims.

What is claimed is:

1. A composition of matter consisting essentially of, in admixture,

- (a) an aromatic polycarbonate,
- (b) a crystalline aromatic polyester,
- (c) a thermoplastic epoxide-containing copolymer, having a glass transition temperature of less than 0° C., prepared from (i) one or more olefin monomers, and (ii) at least one vinyl monomer carrying at least one epoxide group, and
- (d) a rubber-modified styrene/acrylonitrile copolymer containing 1 to 25 percent rubber by weight and optionally a filler.

2. The composition of claim 1 wherein the rubber portion of the styrene/acrylonitrile copolymer comprises one or members of the group consisting of a butadiene, ethylene/propylene/diene copolymer and an alkyl acrylate.

3. The composition of claim 1 wherein the rubber-modified styrene/acrylonitrile copolymer is a mass produced acrylonitrile/butadiene/styrene copolymer.

4. The composition of claim 1 wherein the rubber-modified styrene/acrylonitrile copolymer is a mass produced acrylonitrile/EPDM/styrene copolymer where EPDM is ethylene/propylene/diene copolymer.

5. The composition of claim 1 wherein the rubber-modified styrene/acrylonitrile copolymer contains 1 to 20 percent rubber by weight.

6. The composition of claim 1 wherein the rubber-modified styrene/acrylonitrile copolymer contains 1 to 10 percent

rubber by weight.

7. The composition of claim 1 which contains a filler.

8. The composition of claim 7 wherein the filler is talc, clay, mica, glass or a mixture thereof.

9. The composition of claim 1 in the form of a molded article.

10. The composition of claim 1 wherein component (c) further comprises (c) (iii) at least one vinyl monomer not carrying an epoxide group.

11. The composition of claim 10 wherein component (c) (iii), at least one vinyl monomer not carrying an epoxide group, is grafted as a polymer chain to component (c), the epoxide-containing copolymer.

12. The composition of claim 11 wherein said grafted polymer chain comprises styrene, acrylonitrile, vinyl acetate, methyl methacrylate, or a mixture thereof.

13. The composition of claim 10 wherein the rubber portion of the styrene/acrylonitrile copolymer comprises one or members of the group consisting of a butadiene, ethylene/propylene/diene copolymer and an alkyl acrylate.

14. The composition of claim 10 wherein the rubber-modified styrene/acrylonitrile copolymer is a mass produced acrylonitrile/butadiene/styrene copolymer.

15. The composition of claim 10 wherein the rubber-modified styrene/acrylonitrile copolymer is a mass produced acrylonitrile/EPDM/styrene copolymer where EPDM is ethylene/propylene/diene copolymer.

16. The composition of claim 10 wherein the rubber-modified styrene/acrylonitrile copolymer contains 1 to 20 percent rubber by weight.

17. The composition of claim 10 wherein the rubber-modified styrene/acrylonitrile copolymer contains 1 to 10 percent rubber by weight.

18. The composition of claim 10 which contains a filler.

19. The composition of claim 18 wherein the filler is talc, clay, mica, glass or a mixture thereof.

20. The composition of claim 10 in the form of a molded article.

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